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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

Mathematical Modeling of the Role of Chemical Speciation on Electrokinetic Transport of Chemicals in Soil

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Introduction

Electrokinetic (EK) transport of pollutants from soil consists of the mobilization of species by the application of an external electric DC field.

In EK processes (Fig. 1) the electric current is transported by the ions in the pore solution, which move towards the electrode of different charge (electromigration). Non-ionic species are also mobilized due to electroosmotic advection, i.e. the transport of the pore solution itself under the gradient of electrical potential. In certain conditions, the chemical diffusion can play an important role in the transport process.

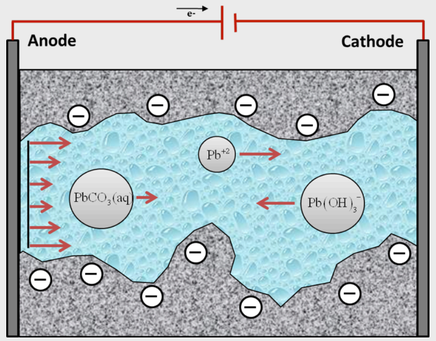

Figure 1: Electrokinetic transport process.

The efficiency of the EK soil remediation treatments was demonstrated to be dependent upon the chemical reactivity of the target pollutants rather than their migration rates. The contaminants have to be in a soluble species, preferably as ionic form, in order to be mobilized under the gradient of electrical potential induced in the system. Heavy metals easily precipitate as insoluble minerals (Fig. 2). In those conditions, the removal rate decreases while the energy consumption increases.

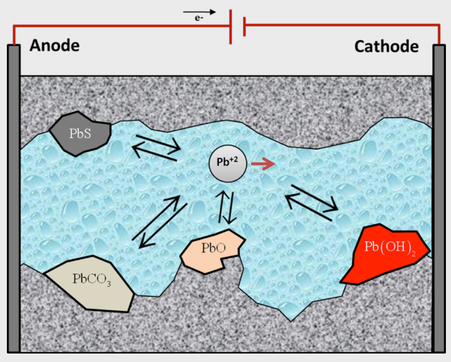

Figure 2: Feasible precipitation/dissolution equilibria for lead minerals during electrokinetic treatments.

Materials and Methods

In the present work, a mathematical model for chemical equilibrium calculation is developed and used for the analysis of the interactions between the species in the pore solution and the solid matrix in lead contaminated soil. The model is based on the simultaneous solution of a set of non-linear equations describing the reversible aqueous and precipitation/dissolution chemical reactions. A tailor-made line-search Newton-Raphson method, iterating on the extent of each reaction, is used to minimize the residual function; defined as the distance to the equilibrium state in the mass action equation of each chemical reaction included in the system.

Table 1: Solubility products of some lead minerals

Stoichiometric reaction	$\log_{10}(K_{SP})$*
$PbS\ (s) \rightleftarrows Pb^{+2} + HS^- - H^+$	-14,84
$PbO \rightleftarrows Pb^{+} + H_2O - 2H^+$	12,62
$Pb(OH)_2\ (s) \rightleftarrows Pb^{+2} + 2H_2O - 2H^+$	8,15
$PbCl_2(s) \rightleftarrows Pb^{+2} + 2Cl_2^-$	-4,81
$PbCO_3(s) \rightleftarrows Pb^{+2} + CO_3^{-2}$	-13,29

Table 2: Equilibrium constants of some lead aqueous compounds

	$\log_{10}(K_{eq})$* as function of x			
	1	2	3	4
$Pb^{+2} + xOH^- \rightleftarrows Pb(OH)_x^{2-x}$	-7,51	-16,95	-27,20	-38,90
$Pb^{+2} + xCO_3^{2-} \rightleftarrows Pb(CO_3)_x^{2-x}$	7,00	10,13	-	-
$Pb^{+2} + HCO_3^{2-} \rightleftarrows PbHCO_3^{+}$	13,20	-	-	-
$Pb^{+2} + xNO_3^- \rightleftarrows Pb(NO_3)_x^{2-x}$	1,06	1,48	-	-
$Pb^{+2} + x\text{Acetate}^- \rightleftarrows Pb(\text{Acetate})_x^{2-x}$	2,78	4,08	3,59	3,40
$Pb^{+2} + x\text{Citrate}^{-3} \rightleftarrows Pb(\text{Citrate})_x^{2-3x}$	7,27	6,53	-	-
$Pb^{+2} + xCl^- \rightleftarrows Pb(Cl)_x^{2-x}$	1,44	2,00	1,69	1,40

The electric current applied is transformed to an ionic current by means of the electrochemical reactions at the electrodes. Electrolysis of water reactions are always likely to happen. Consequently, sharp pH profiles are expected in EK treatments.

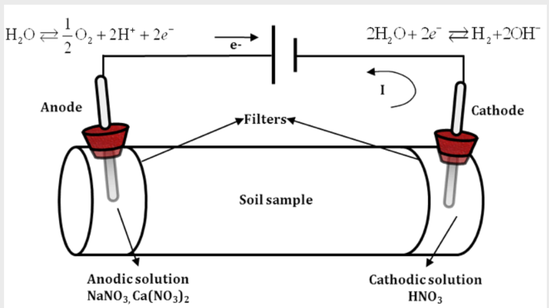

Figure 3: Typical experimental setup for a lab-scale acid-enhanced electrokinetic remediation treatment of a soil sample in horizontal column.

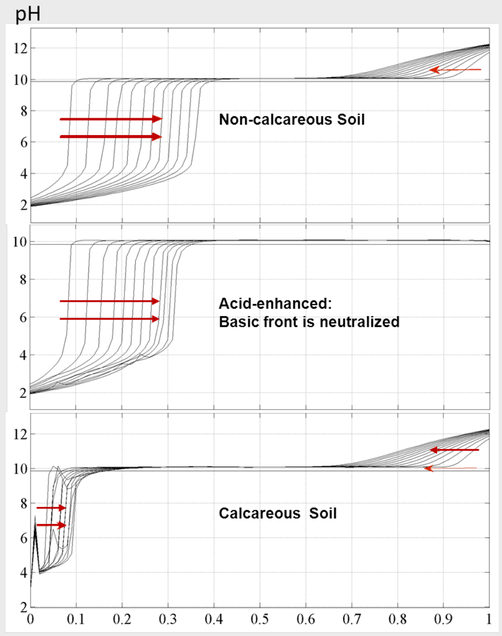

Figure 4: pH profiles from simulations with a Poisson-Nernst-Planck transport model. Constant current 1 mA. 12 hours treatment, one profile per hour. a) non-calcareous soil b) Acid enhanced treatment c) calcareous soil.

I. The acid front that is developing at the anode promotes the desorption and mobilization of most heavy metals during the remediation process.

II. Hindering the basic front developed in the cathode assures acid media in the whole domain and promotes a better mobilization of the contaminants.

III. The buffer capacity of the soil, typically due to the carbonate content, significantly affects the advance of the acid front. Additionally, the formation of insoluble carbonates, such as $PbCO_3$ may be an important type of retention of the heavy metals in calcareous soils.

Extracting agents are used to increase the solubility of the target contaminant, by balancing the equilibrium to the formation of aqueous complexes. The technique can be combined with the acid-enhanced procedures for an efficient and more selective removal of contaminants.

Different extracting agents have been tested to enhance the electrokinetic removal of lead, such as EDTA, acetic acid, citric acid and nitric acid (Table 2).

Results

Simulations presented (Table 3) show the behavior of the chemical system with respect to the buffering capacity of the soil and the pH changes of the pore solution induced by the electrode reactions. Additionally, the role of some extracting agents in the speciation of lead is discussed. Simulations consist of computing the concentration of aqueous species by considering the equilibrium state of pure water (or the specified electrolyte at 0.01 M) and a solid matrix containing enough mineral, that dissolves until over-saturated equilibrium conditions.

Table 3: Simulation results. a) Non-calcareous soil. b) calcareous soil.

		pH	Pb^{+2} [mol/L]	Lead compounds [mol/L]	
				Ionics	Non-ionics
a)	PbS	7.00	1.4783×10^{-11}	1.9347×10^{-11}	1.6568×10^{-14}
	PbS + HAc	468	2.4619×10^{-9}	2.5024×10^{-9}	1.2887×10^{-14}
	PbO	7.48	9.2789×10^{-8}	1.8020×10^{-7}	9.6887×10^{-10}
	PbO + KCl	7.38	1.0076×10^{-7}	1.0076×10^{-7}	6.2621×10^{-19}
	PbO + HAcetate	5.82	9.5024×10^{-6}	9.8358×10^{-6}	9.3012×10^{-11}
	PbO + H_3Citrate	5.92	1.0059×10^{-5}	3.0733×10^{-5}	7.7083×10^{-11}
b)	PbS	9.90	4.4489×10^{-13}	4.4489×10^{-13}	2.4307×10^{-19}
	PbS + HAc	5.68	2.1850×10^{-11}	2.1850×10^{-11}	2.4307×10^{-19}
	$PbCO_3$	8.14	2.2960×10^{-9}	1.2141×10^{-8}	6.9923×10^{-10}
	$PbCO_3$ + KCl	8.12	8.8100×10^{-9}	5.3683×10^{-8}	5.1436×10^{-7}
	$PbCO_3$ + HAcetate	8.12	8.9228×10^{-9}	5.4088×10^{-8}	5.1436×10^{-7}
	$PbCO_3$ + H_3Citrate	6.35	4.4241×10^{-8}	5.6458×10^{-6}	8.4370×10^{-10}

Results from simulations shown that acid enhanced methods, combined with the used of some extracting agents will increase the efficiency of the treatment. In calcareous soil, the buffer capacity limits the acid enhanced applicability.

Conclusion

In the present study a mathematical model for the solution of a set of simultaneous reactions in a multicomponent-multiphase chemical system under the assumption of chemical equilibrium is described. The model used here can be included in a more general model for electrokinetic transport accounting for the chemical reactivity.

Simulations shown the effect of the pH, the initial speciation of the target contaminant, and the influence of the different extracting agents and the soil buffering capacity on the aqueous concentration of the contaminant in the pore solution, which determine the efficiency of the treatment (in terms of the removal rate and the energy consumption).

Acknowledgments

This program is supported by Award Number P42ES017198 from the National Institute of Environmental Health Sciences, USA. Juan Manuel Paz-Garcia acknowledges the Danish Agency of Science Technology and Innovation, for the economical support in the project 274-08-0386 “Fundamentals of Electrokinetics in In-homogeneous Matrices”.